Two-dimensional materials and their usage for renewable energy storage devices

Veera Juntunen

BSc thesis

Physics

Faculty of Natural Sciences

UNIVERSITY OF OULU

December 10, 2019

Supervisor: prof. Matti Alatalo

Contents

1 Introduction

Two-dimensional (2D) materials are one atom thick layers of crystalline solids, which have high ratio between their lateral size and thickness [1]. Since the isolation of graphene, which is a single layer graphite, in 2004 2D materials have been one of the most widely studied classes because of the unusual properties that arise when heat and charge transfer is limited to a plane [2] [3].

Recently energy conversion and energy storage have become a global concern due to the usage of scarce fossil fuels and human-induced global warming. There is a critical need to make use of renewable energy resources, such as solar, wind, and geothermal energy [3]. Thus, researchers are working hard to construct new and alternative choices for energy source devices which are sustainable and environmentally friendly [4] [5]. This leads to the need of rechargeable energy storages to store the electricity generated from sustainable energy sources. Even though current demand for scalable and economic electricity storages is not satisfied, more effort is still needed to create advanced electrode materials with higher energy and power densities [3] [5]. Because 2D materials cover the full range of electronic properties (Fig 1.) [6], it is well justified to go through their suitability for better energy storage devices.

My BSc thesis is a literature review of articles related to this topic. We will discuss about 2D materials in general, their properties and how we could potentially use those materials in more sustainable and better energy storages. In this thesis, we will focus on graphene related materials and transition-metal dichalcogenides because of their interesting electronical properties and possible suitability for future energy storages.

2 Theoretical background

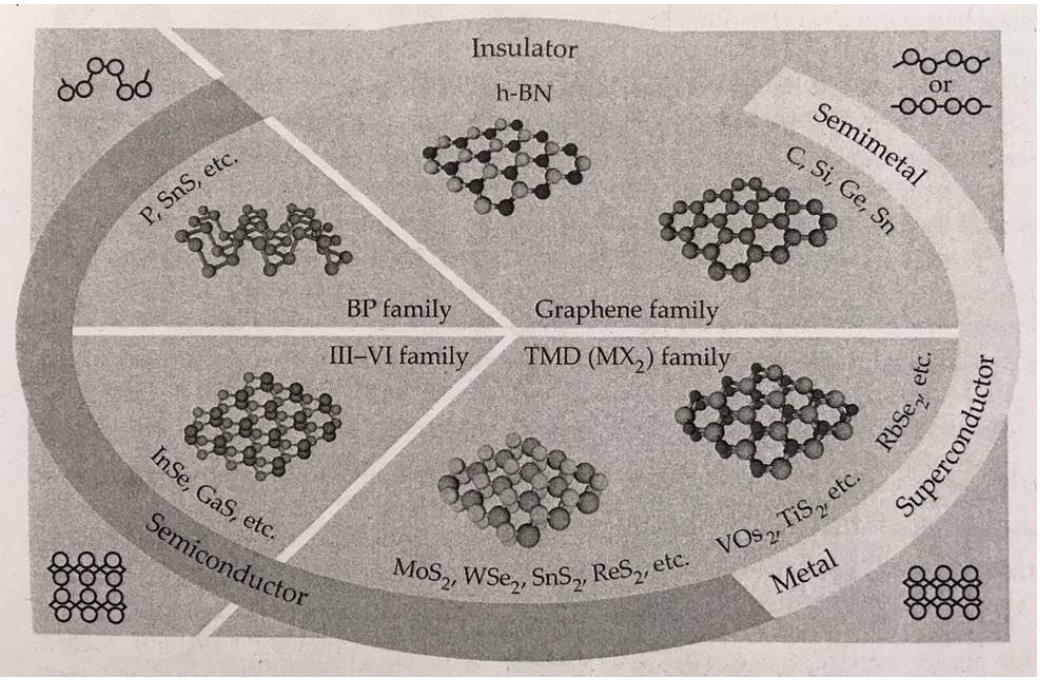

Figure 1: Characterization of different 2D materials. Figure from ref. [6].

2.1 Electronic band structure

Electrons feel the Coulomb potential that is caused by the positive charge of the nucleus. Thus, electrons of a single, isolated atom occupy atomic orbitals that have discrete energy levels. Pauli exclusion principle states that no two electrons can share the same quantum number in a molecule, so when two or more atoms are combined, also each of their atomic orbitals split in two or more molecular orbitals without any of them having the same energy. [7]

When a large number of atoms construct a solid, also every atomic orbital splits into a large number of molecular orbitals. In crystalline materials the ions form a periodic potential, which leads to the separation of regions where electrons can be. Outermost molecular orbitals that are very close in energy

overlap with each other forming energy bands. Between these energy bands are band gaps, which are forbidden energies as a result of the finite widths of the energy bands. [7]

Electrons occupy the energy bands starting from the lowest energy and filling the energy levels until a certain energy, which is called fermi level, ϵ_F. Energy bands below and above the Fermi level are called valence band and conduction band, respectively. The position of Fermi level related to the energy bands determines the electrical properties of material, which is illustrated in figure 2. Metals and semimetals have either large or small overlap between valence band and conduction band, respectively. Semiconductors have a band gap of 1-4eV and insulators >4eV, respectively [8].

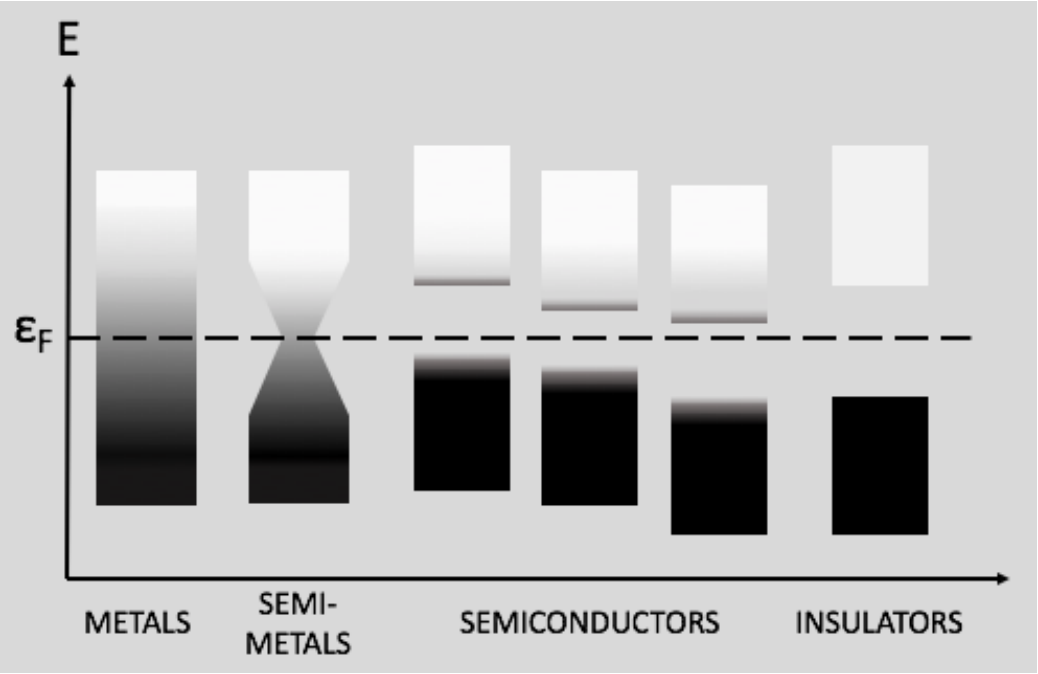

Figure 2: Illustration of Fermi level and how the position in relation to conduction band and valence band affects to the electrical properties of the material. Valence band is the energy band below fermi level and conduction band is the energy band above fermi level.

2.2 Quantum confinement, dielectric screening and interlayer coupling

It is assumed that quantum confinement, dielectric screening and interlayer coupling play an important role in the unique properties of 2D materials. Quantum confinement is a phenomenon, where energy levels of a solid change from continuous to discrete. It can be observed when the diameter of the material is the same magnitude as de Broglie wavelength. [8]

Dielectric screening represents the damping of the inner electric field of the material. Thus, confining the dimensionality of a material leads to reduced dielectric screening and discrete energy levels, which is why we can expect an increase of the band gap and the exciton binding energy. [8] This is illustrated in figure 3. Exciton is a neutral quasiparticle, which is formed from the Coulomb attraction between a negative electron and a positive electron hole. This bound state is thought to transport energy for example in insulators and semiconductors without transporting net electric charge.

Interlayer coupling is a coupling effect that takes place between layers and it reflects the interactions between those layers. Since reducing the dimensionality affects the interactions between layers, interlayer coupling has a significant effect in the mechanical and electronic properties of materials. [8]

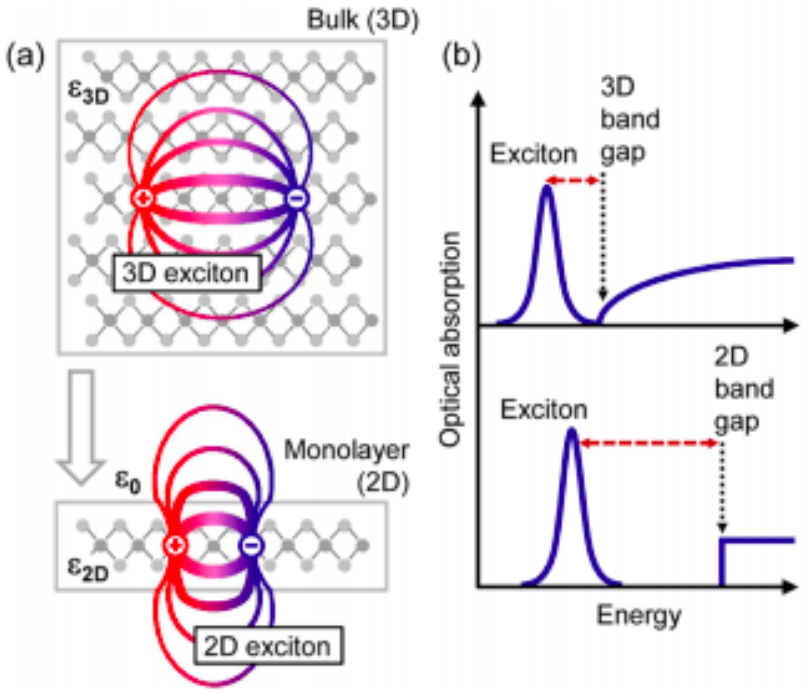

Figure 3: Increase of the band gap and the exciton binding energy of the 2D materials due to quantum confinement and reduced dielectric screening. Figure from ref [8].

3 Two-dimensional materials

One way to define 2D materials is to categorize them as materials whose free charges are fixed in one dimension, but mobile in the other two [4]. Those materials are exfoliated from bulk crystals, which have layered structure due to strong intralayer covalent bonding and relatively weaker interlayer van der Waals interaction [8]. Individual layers can be removed by breaking the van der Waals bonds, causing little damage either to the extracted layer or to the remaining structure [6].

2D materials with their unusual properties have attracted the interest of

scientists, which is due to band gap transitions as the size of the material is reduced. Due to quantum confinement and the strong interlayer coupling, electronic band structure, and hence the properties, of most 2D materials is thickness-dependent [8] and reducing the dimensionality of a system is associated with exceptional properties [6].

3.1 Characterization

2D materials are sorted to different families based on their crystal structure, which is illustrated in Figure 1. Families are graphene related materials (GRMs), transition-metal dichalcogenides (TMDCs), black phosphorous (BP) with its analogues and III-VI family. Monolayer graphene and hexagonal boron nitride (h-BN) are the only 2D crystals where all the atoms occupy the same lattice. Other single-element 2D materials, such as phosphorene, form buckled structures. TMDCs are the group of hexagonal structured materials with the molecular formula MX_2, where M = transition metals and X = chalcogen. TMDCs are three atoms thick and consist of X-M-X sandwich. [6] [9] [8] The existence of over 50 stable 2D TMDC materials have been predicted from density functional theory calculations [10]. More detailed crystal structures of graphene, phosphorene, and molybdenum disulfide (MoS_2) are shown in figure 4b-d.

Common phases for TMDCs are 1T, 2H and 3R. Here 1, 2 and 3 represent the number of unit cells in the direction of c-axis. T, H and R represent the crystal symmetry where T is tetragonal, R is rhombohedral and H is hexagonal. The most common TMDC phases, semiconducting 2H and metallic 1T, are illustrated in figure 4e. [9] [8]

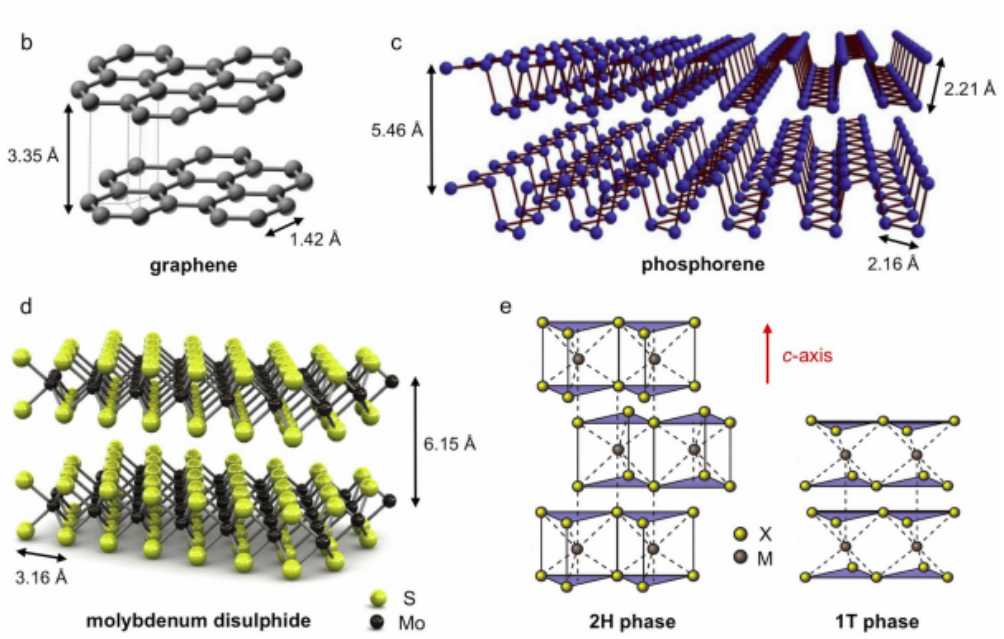

Figure 4: b,c,d, Crystal structures of graphene, phosphorine, and MoS_2 bilayers, respectively. e, Schematic of the most common TMDC phases. Figure from ref. [8].

3.2 Band structure of 2D materials

2D materials have a wide range of physical, chemical and mechanical properties, some of which are suitable for applications in electronics, photonics, composites, and energy storage. Based on their structural configurations and chemical compositions, 2D materials can be classified as metallic, semimetallic, or semiconducting. Compared to 3D bulk materials, their extraordinary properties arise from reduced dimensionality and diminished electric-field screening, which again leads to enhanced quantum effects. Since the electronic band structure affects the electronic properties of a material, it is useful to simplify the electronic band structure in the case of 2D materials by introducing the quasi-relativistic particles near the corners of the first

Brillouin zone (marked as K and K'), as illustrated in figure 5. [6]

Quasi-relativistic particles are illusory systems that behave like relativistic particles. Quasiparticles are used to simplify microscopically complicated systems, and for example electron holes are well known quasiparticles. The first Brillouin zone is a unit cell corresponding to a single lattice point in the reciprocal (or momentum) space. Reciprocal lattice is formed as a Fourier transformation from a direct lattice, such as Bravais lattice.

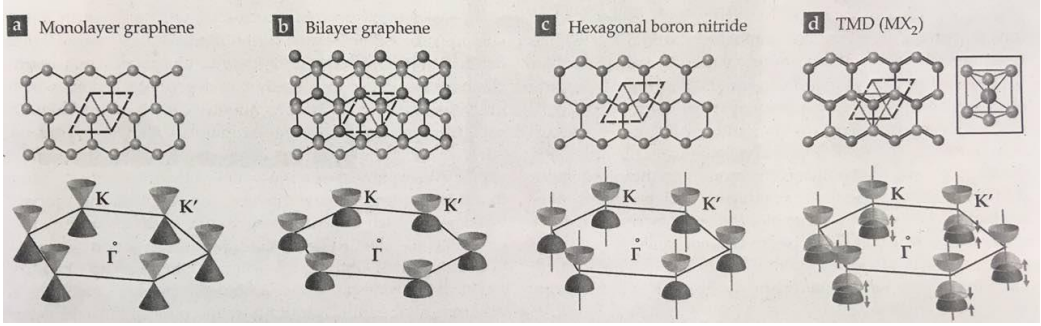

Figure 5: Lattice structure and electronical band structures at the corners of the Brillouin zone. Figure from ref. [6].

In figure 5a the valence and conduction bands of a graphene meet in conical valleys. Here energy is represented in the vertical dimension and momentum in the horizontal dimension, therefore energy is directly proportional to momentum and quasiparticles travel like massless electrons. [6]

When two graphene layers are stacked together, they form a honeycomb lattice. Now the energy dispersion becomes parabolic, quasiparticles gain a mass and the inversion symmetry prevents the band gap from opening, as seen in figure 5b. By breaking up the inversion symmetry the dispersion can be lifted up, which opens up the band gap at the valley. As figure 5d shows, TMDCs' crystal structure causes that they have no inversion symmetry and therefore most of them have nonzero band gaps. [6]

3.3 Synthesis

There are several methods to synthesize 2D layered nanostructures and their hybrids. Some of the best known methods are presented in figure 6. They are categorized either as top-down or bottom-up methods. In the top-down methods 2D nanostructures are exfoliated from bulk crystals by applied forces. In bottom-up method 2D nanostructures are synthesized from the precursors. [4]

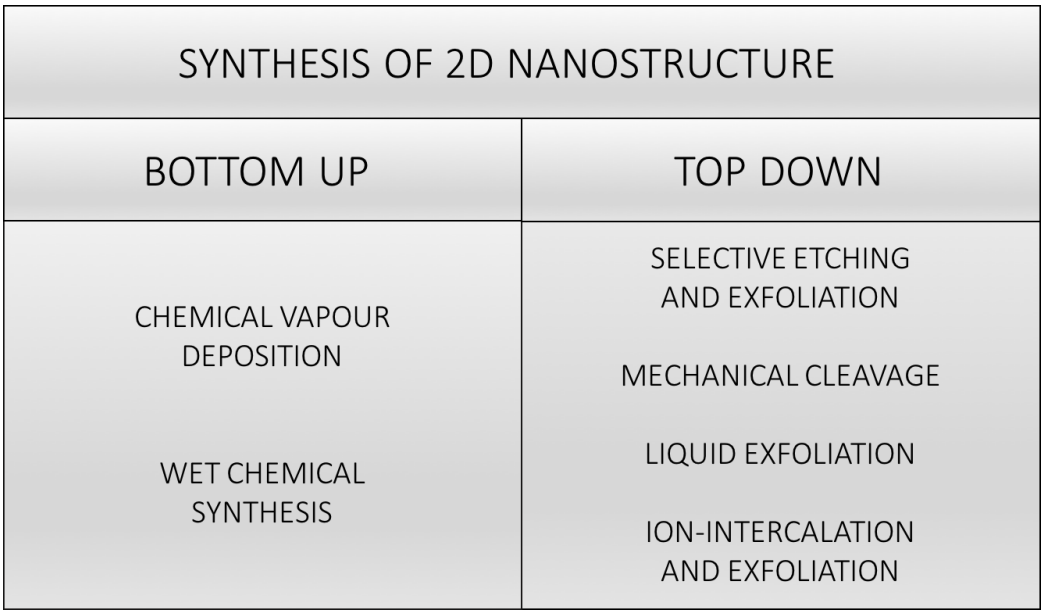

Figure 6: Illustration of several 2D material synthesis methods. Figure is based on reference [4].

Mechanical cleavage, wet chemical synthesis and chemical vapor deposition are among the most used techniques for the preparation of ultrathin 2D sheets of our interests. Mechanical cleavage is the famous "Scotch-tape" technique which was used in graphene exfoliation back in 2004 [4]. In this technique a lateral force is focused on the surface of bulk material by a simple scotch tape to break the relatively weak interplanar van der Waals forces.

After the isolation, the single- and few-layered sheets can be placed on substrates. This technique has been successful in the exfoliation processes within the group of TMDCs. Nowadays this method has become popular due to its versatility and low cost. [9] [10] In wet chemical synthesis 2D nanostructures are created via chemical reactions and deposition of substrates. It is a low-cost room temperature bottom-up process for TMDC materials. However, the starting materials and synthesis approaches vary depending of the type of the material. [9]

Unlike the previous method, chemical vapor deposition is a high temperature chemical synthesis process. This method was recognized for 2D nanostructure synthesis when large scale monolayer graphene on copper foil was successfully demonstrated by this synthesis process. It has also been used for synthesis of large scale TMDC materials. [9]

3.4 Van der Waals heterostructures

Van der Waals heterostructures are layered combinations of different 2D materials with atomically sharp interfaces between the layers. By stacking these materials it is possible to construct desirable hetero architectures with entirely new functions. Tuning the twisting angle between layers gives more freedom to engineer 2D-2D composite materials, since only at particular discrete twisting angles between layers the two lattices form a periodic structure. This non-periodic stacking would cause porous structures in the composite materials, which leads also to different interlayer coupling interactions between dissimilar stacking configurations. [6][10]

After separation and possible post treatment of single 2D materials, the desired 2D layered composites are created. There are a couple of suggested preparation methods, which we will go through briefly just to name a few.

The exfoliation method for chemically exfoliated products is very convenient for the preparation of 2D-2D hybrids, according to Xi Wang et al [10]. By this method it is possible to maintain the in-plane structural integrity of 2D nanosheets, and it is also suitable for scalable production. One other way to prepare 2D-2D composites is hydrothermal growth, which is a crystallizing technique. It is an efficient method especially for few-layered TMDC materials. [10]

4 Energy storages

Systems for electrochemical energy storages include batteries, fuel cells and electrochemical capacitors (i.e. supercapacitors). Even though they all have electrochemical similarities, which are that the energy providing processes take place at the phase boundary of the electrode interface and that electron and ion transport are separated, their energy storage and conversion mechanisms are different. [11] In this thesis, we will focus on batteries and supercapacitors.

Figure 7 illustrates basic elements of batteries and supercapacitors. On the left is a picture of a Daniell cell, which is a commonly used cell in batteries. In a Daniell cell anode and cathode are placed in different electrolytes which are separated by a separator. The battery consists of one or more similar cells connected either in parallel or series. On the right is a picture of a supercapacitor. Supercapacitors consist of two electrodes, separated by a separator, that are connected ionically via an electrolyte.

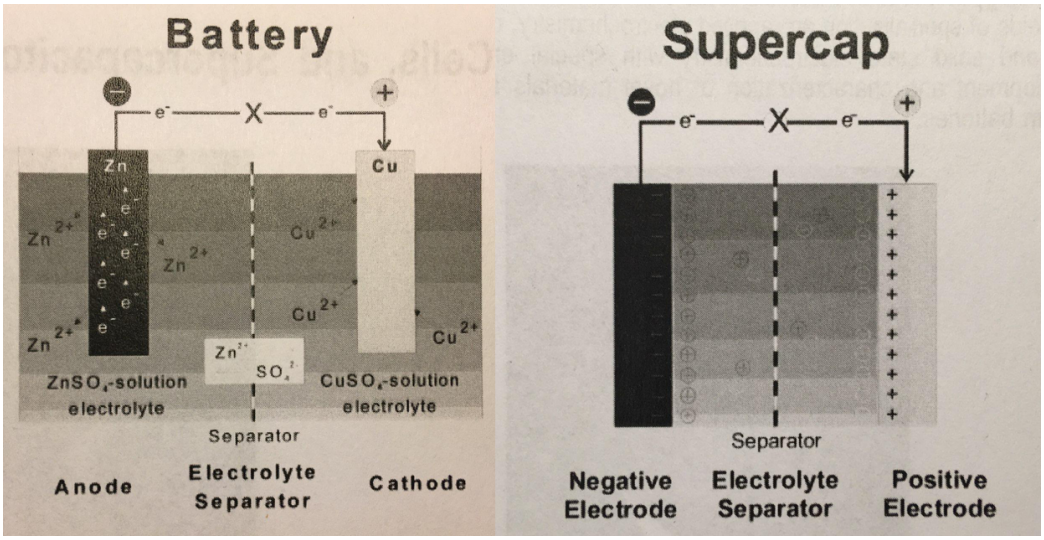

Figure 7: Representation of a battery and a supercapacitor. Figure from ref [11].

Batteries are devices, where electrical energy is generated by the Faradic redox reactions at the anode and cathode. [4] Redox is shortened from reduction-oxidation reaction, which means that one atom hands over an electron to another atom, which leaves the atom either reduced or oxidized. The difference between batteries and fuel cells is based on the locations of energy storage and conversion. Batteries are closed systems, where electrodes take an active role and energy storage and conversion occur in the same section, whereas fuel cells are open systems, where electrodes work as a charge-transfer media and thus energy storage and conversion are locally separated. [11]

Supercapacitors store energy via electrical double layer effect, which happens at the interface of electrode and electrolyte. It is a structure where, for example, the surface charge of negatively charged electrode attracts the positive ions of the electrolyte via the Coulomb force. In some cases, redox reactions at electrode materials are also responsible for charge storage. [4]

Current use of rechargeable energy storages requires light-weight and flexible materials, which are properties that must be noticed in order to reach a global market and thus fulfill the demand for environmentally friendly option. Based on the working methods of batteries and supercapacitors, we are looking for materials with high energy density ($\mathrm{Wh\,kg^{-1}}$), high power density ($\mathrm{kW\,kg^{-1}}$) and large surface-to-mass ratio ($\mathrm{m^2 g^{-1}}$). Large surface-to-mass ratio allows the material to store and release either ions or electric charge, in the case of batteries or supercapacitors, respectively. [5]

Other desired properties describe the quality of the electric storage, which are the capacity of a battery ($\mathrm{Ah\,g^{-1}}$) and a cyclic lifespan of the electrode material. [10] The capacity of a battery describes the amount of electric charge it can deliver in a measured time unit. Since the capacity is dependent on the amount of the material itself, it is justified also from this point of view to seek for lighter electrode materials. For rechargeable batteries, battery lifetime is measured in cycles. In here, the amount of cycles is the number of charge-discharge cycles that are possible before the battery cells fail to work as desired.

Most of the current rechargeable energy storages are lithium-ion based batteries, where the material used for anode is graphite. Lithium-ion batteries are widely used because of their respective high energy density, no memory-effect and a long lifespan [10]. As for a comparison, the most common lithium-ion batteries with graphite have a capacity of 372 $\mathrm{mAh\,g^{-1}}$ [10], a lifespan over 500 cycles, a theoretical energy density of 387 $\mathrm{Wh\,kg^{-1}}$ and a measured energy density of 120 to $\sim$150 $\mathrm{Wh\,kg^{-1}}$ [5].

Beyond graphite, few examples for other possible anode materials in lithium-ion batteries are silicon, phoshorus and sulphur. However, there are still challenges related to these high-capacity anodes - poor electrical con-

ductivity and a possible break of the electrodes, which is caused by the large volume changes during cycling. [10]

The total stored energy for each electrode material can be separated into three different phenomena; the diffusion controlled insertion/de-insertion process; the surface capacitive effects; and non-Faradaic contribution caused by a double-layer effect. In the case of traditional lithium storage materials the latter two can be ignored. However, those two capacitive components must be taken account in electrodes made of 2D materials because of the extremely large surface areas. [10]

5 2D materials in energy storages

During the past decade inorganig TMDC materials and their composites have shown desirable features for electrode materials in lithium-ion and sodium-ion batteries. Even though high capacities, good cycling stabilities and high-rate capabilities give promising expectations, Xi Wang et al. are emphasizing that TMDC-based battery performances are varying, indicating many unknown factors related to the issue [10]. However, it has been found that battery performances of TMDC materials can be improved by hybridization of different 2D materials. This is especially true with hybrids based on graphene and other 2D materials, since their in-plane lattice mismatch between layers leads to the formation of layer distortions, void/pore structures and many exposed active sites. [10]

5.1 Potential materials and their electrical properties

Xi Wang et al. mention a few potential 2D material choices for a new era electrodes to use as such or as a part of a composite. One of the most promising

electrode material for rechargeable batteries is graphene and graphene based materials, such as nitrogen doped graphene [10]. Graphene, and also MoS_2, have electrical properties that are better for batteries compared to the properties they have in 3D form. Graphene is famous for its excellent electrical properties, but it also has zero energy band gap and quite dreadful degradation of carrier mobility, which can be affected by doping and creating 2D-2D composites. [9] For example, N-doped graphene has been found to exhibit higher rate capability and capacity for lithium storage than pure graphene, which has been shown to deliver reversible capacities of 794-1054 mA h g^{-1}. [10]

On the other hand, 2D MoS_2 and its hybrids are interesting possibilities for battery community since they could be used for a design of operational devices with minor safety concerns [10]. MoS_2 has a band gap of $\sim$1.8eV and mobility of $\sim$200$cm^2V^{-1}s^{-1}$. Comparing this to graphene in this context shows the advantages of MoS_2, since there is no need for doping or making extremely narrow ribbons to create a well-suited band gap. [9] It has also been demonstrated that MoS_2 can act as pseudocapacitive energy storage material with a specific capacity of 173 mA h g^{-1} for lithium-ions [10].

5.2 Microscopic mechanisms

Different nanostructures have been studied with various microscopic methods, including transmission electron spectroscopy, which makes it possible to study the structural evolution of a nanostructured electrode at near-atomic or atomic resolutions in real time. Comparisons between nanostructures have shown that mechanical degradation and electrochemical reaction are material-specific, size-dependent, and geometry- and composition sensitive. Xi Wang et al. have presented the four different microscopic mechanisms of

nanostructured electrodes, which are classified based on their differences in electrochemical energy storage pathways and mechanisms during charging-discharging. Those four categories are; intercalation/de-intercalation mechanisms; alloying/de-alloying mechanisms; conversion storage mechanisms; and surface capacitive adsorption/desorption mechanisms. [10]

Considering rechargeable batteries, one of the most important anode types are intercalation/de-intercalation-based anodes. Those could be made of materials such as graphite, graphene, or MoS_2. Experiments with electrodes made of few-layer nanoribbons (GNRs) and lithium have shown that during lithiation the surfaces and edges of GNRs are covered with Li_2O, and most Li_2O is removed during delithiation, which suggests that the lithiation/delithiation processes occur mainly at the surfaces and a possible solid electrolyte interface (SEI) layer is formed [12]. In GNRs the unconfined stacking of planar carbon layers allow the ease of insertion/deinsertion of Li^+ ions into the graphene layers, since a weak coupling effect can arise in GNRs between the intralayer and interlayer deformations. [10] Upon lithiation, it has also been visualized that the discharging process in N-doped graphene (GN) occurs at the edges, initiated from the edge to the center [13]. In GN the SEI layer has been indentified to be Li_2O [10].

During the first Li-ion intercalation, the evolution of MoS_2 nanosheet has also been visualized. As earlier mentioned in section 3.2, the MoS_2 has two different phases, 2H and 1T, and it has been showed that during lithiation the 2H-MoS_2 changes into the 1T phase. Due to these electron-lattice interactions, a pseudoperiodic structural modulation is formed, which is composed of polytype superlattices. Polytypes are materials which exist in two or more crystal structures but as a stacked system their crystal structure differs only in one dimension. [10]

In many high capacity materials, such as Si, Sn, P, S and Ge, both lithiation and sodiation rely on the alloying/de-alloying mechanisms. Usually this type of anodes suffer from huge volumetric and structural changes during charging-discharging, which leads to poor cycling performance. Several designs have been tested to overcome the problems faced in this type of anodes, but more work is still needed for optimization. [10]

Conversion mechanism based anodes face commercial problems similar to the latter. Its electrochemical working principle is based on the formation and decomposition of Li_2O inside transition metal oxide anodes, such as CuO and Fe_2O_3. During the first cycle an electrolyte decomposition causes the formation of a SEI layer over the active particle surfaces, which results several issues, such as irreversible capacity loss and large volume variation. [10]

Surface capacitive adsorption/desorption mechanism is based on the two inseparable capacitive phenomena mentioned in section 4: the surface capacitive effects (pseudocapacitance) and non-Faradaic contribution caused by a double-layer effect. Due to large surface area of 2D materials, these two phenomena are important to take into account and distinguish from the total storing energy in 2D nanostructure electrodes, since usually many imperfections caused by doping or functional groups exist on the surfaces. For example, graphene delivers high reversible capacities due to surface capacitive effects, which is believed to be caused by highly distorted sp^2 nanodomains. The importance of doping-induced absorption effects in 2D nanostructures has also been studied, and for a few-layered graphene, the charge carriers can either intercalate between layers or adsorb on the surface. Xi Wang et al. mention that in their study they have noticed that N-doped graphene has an enhanced insertion capacity and surface capacitive contribution compared to

graphene, due the distortions caused by doped nitrogen. [10]

6 Summary

The discovery of two-dimensional materials has led to several new research areas in the field of materials science. Since during the last decade the production of environmentally friendly energy storages has been in high demand, also 2D materials have been studied for next generation anode materials. If 2D materials can answer to this demand, it is important to create an electrode material with enhanced safety that is inexpensive to produce, has a scalable size and its electrochemical properties enable the production of better alternatives for current energy storages. A lot of different 2D materials and their composites have been studied in this matter, and this thesis covered only basics of the few potential materials. Still there is a huge need for an extensive basic research of 2D materials to get the full scientific understanding, which will help to develop smarter ways of harnessing the full potential of those materials.

References

[1] X. Cai, Y. Luo, B. Liu, and H.-M. Cheng, "Preparation of 2D material dispersions and their applications," *Royal Society of Chemistry*, vol. 47, pp. 6224–6266, 2018.

[2] S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutiérrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, and J. E.

Goldberger, "Progress, challenges, and opportunities in two-dimensional materials beyond graphene," *ACS Nano*, vol. 7, no. 4, pp. 2898–2926, 2013.

[3] P. Zhang, F. Whang, M. Yu, X. Zhuang, and X. Feng, "Two-dimensional materials for miniaturized energy storage devices: from individual devices to smart integrated systems," *Royal Society of Chemistry*, vol. 47, pp. 7426–7451, 2018.

[4] R. Sahoo, A. Pal, and T. Pal, "2D materials for renewable energy storage devices: Outlook and challenges," *Chemical Communications*, vol. 52, no. 93, pp. 13528–13542, 2016.

[5] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, and V. Pellegrini, "Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage," *Science*, vol. 347, no. 6217, 2015.

[6] P. Ajayan, P. Kim, and K. Banerjee, "Two-dimensional van der waals materials," *Physics Today*, vol. 69, no. 9, pp. 38–44, 2016.

[7] E. Thuneberg, "Solid state physics." Course material, University of Oulu.

[8] M. Velický and P. S. Toth, "From two-dimensional materials to their heterostructures: An electrochemist's perspective," *Applied Materials Today*, vol. 8, pp. 68–103, 2017.

[9] S. Das, M. Kim, J. W. Lee, and W. Choi, "Synthesis, properties, and applications of 2-D materials: A comprehensive review," *Critical Reviews in Solid State and Materials Sciences*, vol. 39, no. 4, pp. 231–252, 2014.

[10] X. Wang, Q. Weng, Y. Yang, Y. Bando, and D. Golberg, "Hybrid two-dimensional materials in rechargeable battery applications and their microscopic mechanisms," *Chemical Society Reviews*, vol. 45, no. 15, pp. 4042–4073, 2016.

[11] M. Winter and R. J. Brodd, "What are batteries, fuel cells, and supercapacitors?," *Chemical reviews*, vol. 104, no. 10, pp. 4245–4269, 2004.

[12] S. Qingmei, Z. Jun, W. Yishan, and D. Gaohui, "Revealing the electrochemical conversion mechanism of porous Co_3O_4 nanoplates in lithium ion battery by *in situ* transmission electron microscopy," *Journal of Materials Chemistry*, vol. 21, no. 22, pp. 8038–8044, 2014.

[13] Z. Luo, S. Lim, Z. Tian, J. S. L. Lai, B. MacDonald, C. Fu, Z. Shen, T. Yu, and J. Lin, "Pyridinic N doped graphene: Synthesis, electronic structure, and electrocatalytic property," *Journal of Materials Chemistry*, vol. 21, no. 22, pp. 8038–8044, 2011.